

Comparison of the reduction behaviour of anodic PbO₂ films on Pb–As and Pb–Bi alloys in sulfuric acid

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The reduction behaviour of the anodic PbO₂ films on Pb-3 at % As and Pb-3 at % Bi has been investigated using *in situ* photocurrent spectroscopy, impedance methods, chronoamperometry and linear sweep voltammetry. The experimental results show that most of the PbO₂ in the film can be converted to PbSO₄ in about 2 s at 1.0 V (vs Hg/Hg₂SO₄). Alloying with both As and Bi slightly retards this reduction process. The remaining PbO₂ can only be reduced at a lower potential, (e.g., 0.60 V vs Hg/Hg₂SO₄) to *t*-PbO. Alloying with As slows down this second reduction process, while alloying with Bi accelerates it markedly.

Keywords: PbO₂ films, Pb–As alloy, Pb–Bi alloy, reduction behaviour

1. Introduction

Loss of cycling capacity, low charge acceptance and low performance in a heavy duty cycle discharge lead–acid battery are closely linked to the structure, properties and phase transformation processes of the corrosion film on the positive grid. To attain a better understanding of such films, many investigations have been conducted on the anodic films formed on lead or its alloys in sulfuric acid solutions since the 1950s [1–6]. However, some apparently fundamental processes at the anodic films are still open to discussion. In our previous photoelectrochemical investigations on the reduction of anodic PbO₂ films formed on Pb and Pb–Sb alloys in H₂SO₄ solutions [7, 8], we proposed that the remaining part of α -PbO₂ could be transformed to PbO_x ($1 < x < 1.4$) and finally to *t*-PbO at an over-discharge potential, in addition to the well-recognized conversion of PbO₂ to PbSO₄, which was designated to take place in the outer layer of the anodic PbO₂ film. Antimony as an alloying additive was found to greatly hamper the overall reduction process of α -PbO₂ to *t*-PbO. Moreover, the higher the content of antimony, the slower such a reduction proceeded. Since *t*-PbO and α -PbO_x exhibit much higher specific resistivity with respect to α -PbO₂ and α -PbO_y ($1.4 < y < 2$) [9–11], these observations may provide insight into the fact that antimony is beneficial to the deep discharge cycling performance, as well as that batteries utilizing

antimony-free or low antimony grids can suffer premature capacity loss [10, 12].

Arsenic and bismuth have been adopted as minor alloying agents for preparation of the grids of a lead–acid battery [1, 13]. In contrast with the systematic and intensive studies of the antimonial effects on the structure, phase formation and conversion as well as the semiconducting properties of the anodic films on Pb–Sb alloys in H₂SO₄, the influences of As and Bi have received far less attention. In previous investigations [14–16], Zhou *et al.* emphasized the significant influence of these two elements on the fundamental semiconducting properties of the passive layers formed on Pb–As and Pb–Bi alloys as well as the reduction behaviour of *t*-PbO in H₂SO₄ solutions. In the present work, this is extended to assess the effects of As and Bi on the reduction process of the anodic PbO₂ films formed respectively on Pb–3 at % As (denoted as Pb–3As) and Pb–3 at % Bi (denoted as Pb–3Bi) in H₂SO₄. An impedance method in conjunction with a photocurrent technique is used to trace *in situ* the reduction processes at both a normal and a deep discharge potential. The concentration of As or Bi in Pb alloys was deliberately raised here to make such effects more notable and comparable as well as to demonstrate the higher safe level for As or Bi in possible battery applications.

2. Experimental details

Pb–3As and Pb–3Bi alloys made from 99.999% pure lead and 99.95% pure As or 99.9% pure Bi were shaped into rods and sealed with epoxy resin leaving a working surface of 0.28 cm² exposed for each

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electrode. Before being subjected to the sulfuric acid medium, the surface of the working electrode was polished mechanically with emery papers and thoroughly rinsed with double-distilled water. A platinum foil served as the counter electrode and an Hg/Hg₂SO₄ containing the same solution as in the electrochemical cell was used as the reference electrode. All potentials are referred to this electrode. Formation and subsequent reduction of anodic PbO₂ films were conducted in a 4.5 M H₂SO₄ solution prepared from AR H₂SO₄ and double-distilled water. Before anodizing, a cathodic polarization at -1.2 V for 20 min was performed to remove any oxidation products formed during pretreatment. The anodic PbO₂ films studied here were grown on the working electrodes at 1.4 V for 1 h.

Chronoamperometry (CA) and linear sweep voltammetry (LSV) were carried out using an EG&G PARC 273 potentiostat-galvanostat interfaced to a computer with a PARC M270 Electrochemistry Analysis Software.

The setup for the photocurrent technique has been described in detail elsewhere [7]. The measurement was performed in a Faraday-shield room using chopped and adjustable monochromatic light of low intensity. (Incident photon fluxes were controlled to be less than $4 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ to minimize photochemically induced changes of the anodic films.) The photocurrent was measured with a PARC 5209 lock-in analyser and converted into quantum yield with respect to the incident radiation.

A.c. impedance measurements were run using the combination of the above potentiostat-galvanostat and a PARC model 5208 lock-in analyser interfaced to a computer with a PARC M388 software. A sinusoidal perturbation with an amplitude of 5 mV at a constant frequency of 1 kHz was used to trace the change of the real and imaginary parts of the impedance for the processes of initial formation and subsequent reduction of the anodic PbO₂ films on Pb-3As and Pb-3Bi.

3. Results and discussion

3.1. LSV and CA

The anodic PbO₂ films on lead alloys at 1.4 V in H₂SO₄ consists mainly of β -PbO₂ and α -PbO₂ as well as some amounts of *t*-PbO and PbO · PbSO₄ [11, 17–19], and the alloying elements may become incorporated into the lattice of the lead oxides to some extent. Figure 1 shows the negative sweeping voltammograms recorded at 20 mV s⁻¹ for the anodic PbO₂ films on Pb-3As and Pb-3Bi formed at 1.4 V in 4.5 M H₂SO₄ for 1 h, respectively. It is well established that peak C₁ corresponds to the reduction of PbO₂ to PbSO₄, while C₄ represents the reduction of PbSO₄ to Pb. Previous study suggested that most of the β -PbO₂ and part of the α -PbO₂ in the anodic PbO₂ film is converted to PbSO₄ within C₁ [7]. Peak C₂, extending from 0.8 to -0.7 V, may be related to the solid state

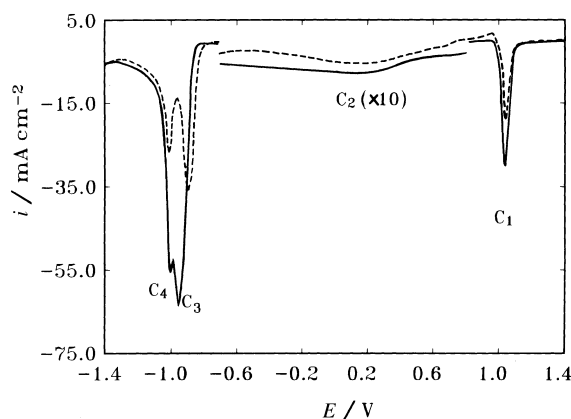


Fig. 1. Negative sweep voltammetry of anodic PbO₂ films formed on Pb-3As and Pb-3Bi respectively at 1.4 V for 1 h in H₂SO₄. Scan rate 20 mV s⁻¹. Key: (---) Pb-3As; (—) Pb-3Bi.

conversion of α -PbO₂ to α -PbO_n ($1 < n < 2$) or PbO_n(OH)_k ($k < 1$) [20]. A previously formed passivation layer of PbSO₄ within peak C₁ hinders the further conversion of the remaining α -PbO₂ to PbSO₄ (*vide infra*). Peak C₃ may be assigned to the reduction to Pb of PbO and PbO · PbSO₄ formed at 1.4 V together with α -PbO_n later produced during LSV. Table 1 compares the reduction charges under C₁ ($-Q_{C1}$) and C₂ ($-Q_{C2}$) for the anodic PbO₂ films on Pb-3As, Pb-3Bi as well as Pb. It can be seen that the reduction charge quantities for both an outer layer of PbO₂ to PbSO₄ and for the remaining α -PbO₂ to α -PbO_n are increased by alloying with Bi and decreased by alloying with As.

In [7], we compared the $(-Q)/t$ plots for the potential step reduction from 1.40 to 1.00, 0.90 and 0.60 V for the anodic PbO₂ films formed on pure Pb. It was found that there existed a maximum reduction charge quantity for each plot (i.e., $(-Q)_{\max}$) at a certain time, t_{\max} . After this, the substrate may be anodized so that $(-Q)$ tends to decrease. Table 2 presents data on $(-Q)_{\max}$, t_{\max} and $(-Q)_{1s}$ ($-Q$ value at 1 s) for the reduction of the anodic PbO₂ films on Pb, Pb-3As and Pb-3Bi at varying final potentials, E_f .

At a discharge potential between 0.90 V and 1.07 V, which is near to the equilibrium potential of PbO₂/PbSO₄ (i.e., ~ 1.085 V) each group of $(-Q)_{\max}$ in Table 2 is close to its corresponding $(-Q_{C1})$ irrespective of the substrate and final potential, although the quantity of PbSO₄ formed to passivate the partially reduced anodic PbO₂ film changes with the substrate. It has been proven that the rule of thin

Table 1. Comparison of the reduction charges for peaks C₁ and C₂ in linear sweep voltammograms for the anodic PbO₂ films on Pb, Pb-3As and Pb-3Bi

Substrate	$-Q_{C1}/\text{mC cm}^{-2}$	$-Q_{C2}/\text{mC cm}^{-2}$
Pb	67	36
Pb-3As	53	26
Pb-3Bi	70	52

Table 2. Comparison of $(-Q)_{\max}$, t_{\max} and $(-Q_{1s})$ for the reduction of anodic PbO_2 films on three types of substrates at various final potentials

E_f / V	Pb			Pb-3As			Pb-3Bi		
	$-Q_{1s}^*$	t_{\max}/s	$-Q_{\max}^*$	$-Q_{1s}^*$	t_{\max}/s	$-Q_{\max}^*$	$-Q_{1s}^*$	t_{\max}/s	$-Q_{\max}^*$
1.07	8	13.7	68	—	—	—	—	—	—
1.05	18	5.04	63	13	5.36	54	15	7.65	65
1.00	66	1.12	66	54	1.51	55	71	2.05	73
0.90	64	0.97	64	54	0.98	54	69	1.04	70
0.80	71	3.20	80	—	—	—	—	—	—
0.60	73	25.0	88	53	28	62	72	34	80

* Unit of $-Q_{1s}$ and $-Q_{\max}$ is mC cm^{-2} .

layer reaction governs the reduction of anodic PbO_2 films to PbSO_4 by a chronoamperometric method. Furthermore, at a reduction potential between 0.90 to 1.00 V, $(-Q_{1s})$ approaches the relevant $(-Q_{\max})$ for each electrode. This also supports the assumption that a thin outer layer of anodic PbO_2 can be almost converted to PbSO_4 within 1 s [7, 8]. $(-Q_{1s})$ tends to decrease with decreasing reduction overpotential. When reduced at a more positive potential (e.g., 1.05 V) both alloying additives slow the above conversion slightly, as can be seen in Fig. 2, where $\eta(\text{PbO}_2/\text{PbSO}_4)$ was defined as $(-Q)/(-Q_{\max})$ in $(-Q)/t$ plots.

However, if the reduction proceeded at a more negative potential, such as 0.60 V, the resultant $(-Q)_{\max}$ was obviously larger than $(-Q_{ci})$, indicating that additional conversion of the remaining $\alpha\text{-PbO}_2$ to $\alpha\text{-PbO}_n$ occurred beneath an outer passivation layer of PbSO_4 [7]. The rapid formation of a semi-permeable layer of PbSO_4 upon reduction results in a higher pH environment for the inner layer of the film [21], lowering the reduction potential of $\alpha\text{-PbO}_2$.

3.2. Photocurrent technique

Since the PbSO_4 passivation layer formed in the outer part of a partially reduced anodic PbO_2 film is transparent, the photocurrent spectroscopy can be used to trace the change of lead oxides in the sublayer

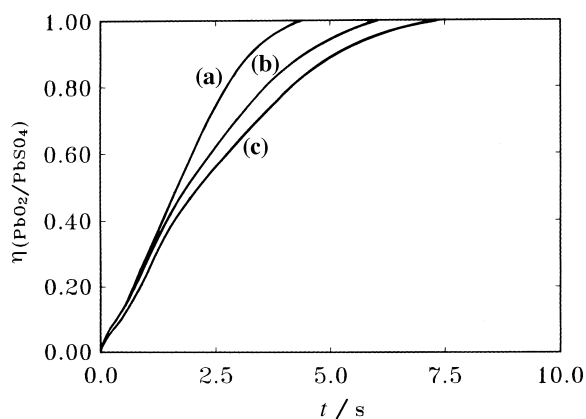


Fig. 2. Time dependence of relative conversion quantity for a layer of anodic PbO_2 to PbSO_4 on (a) Pb, (b) Pb-3As and (c) Pb-3Bi, respectively, when the potential was stepped to 1.05 V.

during reduction. It has been found that the measurability of photocurrent produced by the partially reduced anodic PbO_2 film depends greatly on the reduction potential and time. No photocurrent was detectable if the reduction potential was set at 0.90 V or more positive. With 0.60 V as the reduction potential, it should take about 7, 10 and 5 min for the photocurrent to be detected for the partially reduced anodic PbO_2 films on pure Pb, Pb-3As and Pb-3Bi, respectively.

Among lead oxides, PbO_x ($1 < x < 1.4$) and PbO were reported to be photoactive semiconductors, while PbO_2 and PbO_y ($1.4 < y < 2$) are photoinactive degenerate [11]. It has been deduced that the bandgap energy, E_g , of the photoactive lead oxides can be determined using the following equation, that is,

$$[-h\nu \ln(1 - Y)]^{1/2} = A(h\nu - E_g) \quad (1)$$

where A is a constant, Y the quantum yield, $h\nu$ the incident photon energy [7, 22, 23].

Figures 3 and 4 show $[-h\nu \ln(1 - Y)]^{1/2}$ against $h\nu$ plots for the anodic PbO_2 films reduced at 0.60 V on Pb-3As and Pb-3Bi for different times, respectively. In both cases, E_g , obtained from the intercept of $h\nu$ axis in Figs 3 and 4, increases with reduction time and

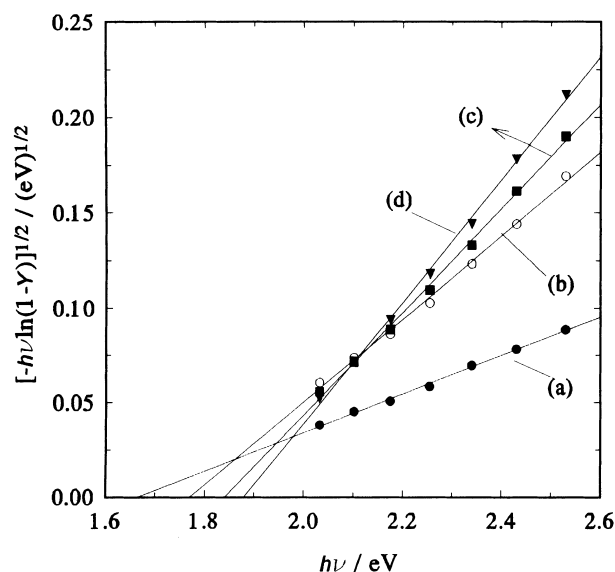


Fig. 3. $[-h\nu \ln(1 - Y)]^{1/2}$ against $h\nu$ plots for the anodic PbO_2 film on Pb-3As reduced at 0.6 V for different times: (a) 20, (b) 45, (c) 75 and (d) 120 min.

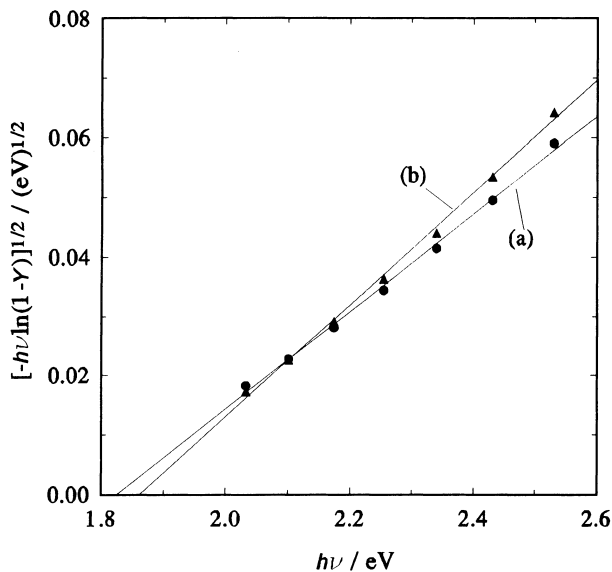


Fig. 4. $[-hv \ln(1 - Y)]^{1/2}$ against hv plots for the anodic PbO₂ film on Pb-3Bi reduced at 0.6 V for different times: (a) 10 and (b) 20 min.

finally approaches 1.88 eV, close to that of *t*-PbO (~ 1.90 eV) [24]. However, the E_g values thus obtained for the anodic Pb(II) films simply formed on both alloys at 0.60 V or 0.90 V are around 1.88 eV, regardless of the anodizing time [22]. This can be attributed mostly to the contribution of *t*-PbO with some incorporation of alloying elements. E_g for the partially reduced anodic PbO₂ films locates between that of α -PbO₂ (1.45 eV) [25] and *t*-PbO formed on both Pb-As and Pb-Bi alloys in H₂SO₄. Izvozhikov [26] has reported that E_g of lead oxides decreases with increasing ratio of the O/PbO. Thus the red-shift of E_g in Figs 3 and 4 may reflect the formation of intermediate lead oxides, α -PbO_x, as a result of the reduction of the remaining α -PbO₂ beneath the PbSO₄ passivation layer. The slower conversion of α -PbO₂ to α -PbO_x, and finally to *t*-PbO, may be controlled by the diffusion of O²⁻ ions with oxygen anion vacancies; the structural similarity among the α -PbO₂, α -PbO_n and *t*-PbO may favour such a conversion [1]. With a higher reduction potential or an inadequate reduction period, the α -PbO₂ may only turn to α -PbO_y, as a result, no photocurrent was sensed.

The most striking difference in the reduction behaviours at 0.6 V, seen from Figs 3 and 4, is that the degradation of the remaining α -PbO₂ on Pb-3Bi to *t*-PbO proceeds much faster than that on Pb-3As, that is, 20 min against 120 min. In comparison with the corresponding results for the Pb electrode (70 min) [7], it can be concluded that Bi speeds up the above process while As suppresses it markedly. It is a very interesting finding that As plays a similar role as Sb in slowing down the formation of highly resistive *t*-PbO at a deep discharge potential. It may open an opportunity for the replacement of Sb with As in fabricating the antimony-free or low antimony grids. On the other hand, the adverse effect of Bi in this respect should also be taken into consideration in battery applications.

As shown in Table 2, after a reduction period of ~ 30 s at 0.60 V or 1 s at 0.90 V, the simultaneous oxidation of substrates may start although such a process is impeded by the existence of a partially reduced anodic PbO₂ film. It can be deduced that the photocurrent technique used here detects mainly the response of the partially reduced PbO₂ film. We have observed that for an identical period of oxidation the anodic Pb(II) film directly formed at 0.90 V in H₂SO₄ exhibits a stronger photocurrent response than that at 0.60 V. In contrast, no photoelectrochemical effect can be measured for the anodic PbO₂ films reduced at 0.90 V despite the fact that the simultaneous oxidation of substrates is a little more conspicuous than that at 0.60 V. These results support the above deduction. Further evidence can be sought from the impedance comparison.

3.3. Impedance measurement

It is very difficult to analyse the transient impedance spectroscopy for such a complex anodic film system; however, using a perturbation signal of unique moderate frequency (i.e., 1 kHz) the measured electrochemical impedance can be represented qualitatively by a resistance, R_s , in series with a capacitance, C_s , where R_s , C_s are mainly related to the resistance and capacitance of the anodic film, respectively. Thus,

$$R_s = Z', \quad C_s = -1/(2\pi fZ'') \quad (2)$$

According to Lappe and Pavlov's suggestion on the dependence of the electronic conductivity of lead oxides on their stoichiometric coefficient [9, 10], a decrease in n in PbO_n may cause an increase in R_s and a decrease in C_s . For clarity, Table 3 only lists the time dependent C_s for anodic PbO₂ films on Pb, Pb-3As and Pb-3Bi reduced at 0.60 V and 0.90 V, while Table 4 compares the relevant C_s for anodic Pb(II) films simply formed at 0.60 V and 0.90 V on the above substrates. (The impedance measurement for the anodic PbO₂ films reduced at a potential ranging from 0.90 to 1.05 V exhibits similar results.)

It turns out that C_s for the anodic Pb(II) film grown at 0.90 V on each substrate is slightly smaller than the corresponding C_s at 0.60 V, which is in accordance with a relatively thicker PbO formed at

Table 3. Comparison of the time dependent C_s for anodic PbO₂ films on Pb-3As and Pb-3Bi reduced at 0.6 V and 0.9 V

t/min	C_s at 0.6 V/ $\mu\text{F cm}^{-2}$			C_s at 0.9 V/ $\mu\text{F cm}^{-2}$		
	Pb	Pb-3As	Pb-3Bi	Pb	Pb-3As	Pb-3Bi
1	13	11	10	1.9×10^2	1.3×10^2	1.3×10^2
10	4.0	4.1	1.8	86	88	74
20	2.0	2.7	0.34	57	67	49
30	0.92	2.0	0.28	45	54	20
40	0.57	1.4	—	38	45	—
50	0.45	1.0	—	33	39	—
60	0.39	0.82	—	30	34	—

* C_s values for anodic PbO₂ films formed on these substrates before reduction are essentially the same, namely, $3.1 \times 10^3 \mu\text{F cm}^{-2}$.

Table 4. Time dependent C_s for the anodic Pb(II) films on Pb-3As and Pb-3Bi formed at 0.6 V and 0.9 V

t/min	C_s at 0.6 V/ $\mu\text{F cm}^{-2}$			C_s at 0.9 V/ $\mu\text{F cm}^{-2}$		
	Pb	Pb-3As	Pb-3Bi	Pb	Pb-3As	Pb-3Bi
1	7.1	6.5	4.7	5.8	4.9	4.0
10	2.4	1.9	1.6	2.0	1.5	1.3
20	1.6	1.3	1.0	1.4	1.1	0.84
30	1.2	1.0	0.82	1.1	0.86	0.65
40	1.0	0.88	0.69	0.89	0.72	0.55
50	0.89	0.77	0.62	0.77	0.54	0.48
60	0.79	0.68	—	0.69	0.50	—

0.90 V than at 0.60 V for a given time. By contrast, in the case of reduction of the anodic PbO₂ films, the reverse situation is observed, that is, C_s at 0.90 V is tens of times larger than the corresponding C_s at 0.60 V, although the simultaneous oxidation of substrates from the time of 1 min on proceeds slightly faster at 0.90 V. A better explanation is that at 0.9 V the remaining α -PbO₂ in the partially reduced PbO₂ film can not be degraded to a higher resistive α -PbO_x and *t*-PbO. Moreover, it can be seen that C_s for the partially reduced anodic PbO₂ film at 0.60 V is comparable with C_s for the anodic Pb(II) film in magnitude. These observations agree well with the conclusion drawn from other techniques that at 0.60 V the remaining α -PbO₂ can still be turned gradually to *t*-PbO via α -PbO_x following the initial rapid formation of a PbSO₄ layer. From Table 3, it is seen that the change of C_s with reduction time at 0.60 V takes place most drastically for the partially reduced anodic PbO₂ film on Pb-3Bi, followed by that on Pb, Pb-3As sequentially. Qualitatively, this is also consistent with the results of the photocurrent technique that Bi accelerates the reduction of α -PbO₂ to *t*-PbO while As retards such a process.

4. Conclusion

The photocurrent spectroscopy, impedance methods and chronoamperometry results illustrate that the reduction behaviour of anodic PbO₂ films at a normal and a deep discharge potential (e.g., 0.90 and 0.60 V) is markedly different. Only at a deep discharge potential can the remaining α -PbO₂ beneath a previously formed PbSO₄ layer be reduced to resistive *t*-PbO via intermediate α -PbO_x ($1 < x < 1.4$).

The alloying additives As and Bi exert a totally different influence on the conversion process of the remaining part of α -PbO₂ to *t*-PbO in the anodic PbO₂ films reduced at a deep discharge potential,

such as 0.60 V in H₂SO₄. The former retards the above process while the latter promotes it. By contrast, both alloying additives suppress slightly the overall reduction rate of the outer part of the PbO₂ to a passivation layer of PbSO₄ when anodic PbO₂ films are reduced at normal discharge potentials, extending from 0.90 to 1.05 V.

Acknowledgements

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References

- [1] D. Pavlov, in 'Power Sources for Electric Vehicles' (edited by B. D. McNicol and D. A. J. Rand) Elsevier, Amsterdam, (1984) p. 111.
- [2] P. Ruetschi, *J. Power Sources*, **2** (1977/1978) 3.
- [3] J. L. Dawson, in 'The Electrochemistry of Lead' (edited by A. T. Kuhn) Academic Press, London, (1970), p. 309.
- [4] K. R. Bullock, *J. Electroanal. Chem.* **222** (1987) 347.
- [5] S. R. Ellis, N. A. Hampson, M. C. Ball and F. Wilkinson, *J. Appl. Electrochem.* **16** (1986) 159.
- [6] T. Laitinen, K. Salmi, G. Sundholm, B. Monahov and D. Pavlov, *Electrochim. Acta* **36** (1991) 605.
- [7] W.-B. Cai, Y.-Q. Wan, H.-T. Liu and W.-F. Zhou, *J. Electroanal. Chem.* **387** (1995) 95.
- [8] *Idem*, *Chin. J. Chem.* **14** (1995) 138.
- [9] F. Lappe, *J. Phys. Chem. Solids* **23** (1962) 1536.
- [10] D. Pavlov, *J. Power Sources* **53** (1995) 9.
- [11] K. R. Bullock and M. A. Butler, *J. Electrochem. Soc.* **133** (1986) 1085.
- [12] D. A. J. Rand, *J. Power Sources* **23** (1988) 269.
- [13] J. D. Lam, T. D. Huynh, N. P. Haigh, J. D. Douglas, D. A. J. Rand, C. S. Lakshmi, P. A. Hollingsworth, J. B. See, J. Manders and D. M. Rice, *ibid.* **53** (1995) 75.
- [14] S.-J. Xia and W.-F. Zhou, *J. Appl. Electrochem.* **24** (1994) 894.
- [15] *Idem*, *Electrochim. Acta* **40** (1995) 181.
- [16] C. Pu, Z.-L. He and W.-F. Zhou, *J. Power Sources* **39** (1992) 233.
- [17] B. K. Mahato, *J. Electrochem. Soc.* **126** (1979) 365.
- [18] N. A. Hampson, S. Kelly, K. Peters and D. Whyatt, *J. Appl. Electrochem.* **10** (1980) 597.
- [19] C. Wei, X.-L. Chen, H.-M. Li and W.-F. Zhou, *Acta Chimica Sinica* **47** (1989) 569.
- [20] D. Pavlov, I. Balkanov and P. Rochev, *J. Electrochem. Soc.* **134** (1987) 2390.
- [21] P. Ruetschi, *J. Electrochem. Soc.* **120** (1973) 331.
- [22] W.-B. Cai, Thesis, Fudan University (1995).
- [23] Yu. V. Pleskov and Yu. Ga. Gurevich, Semiconductor Photoelectrochemistry, Consultants Bureau, New York, (1986).
- [24] D. Pavlov, S. Zanova and G. Papazov, *J. Electrochem. Soc.* **124** (1977) 1522.
- [25] W. Mindt, *J. Electrochem. Soc.* **116** (1969) 1076.
- [26] V. A. Izvozchikov, *Fiz. Tverdogo Tela* **3** (1961) 2060, 3229.